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Project Summary

ORIGINAL

Oil Slick Dispersal Mechanics

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This study investigates the spreading and dissolution behavior of small oil slicks formed from spills of 12 oils. The increases in area covered by the oils during spreading experiments were determined using photographic techniques. Spreading equations were derived and used to correlate experimental data. Derivation of the equations parallels Fay's development.

The rates of dissolution of the oils in tap water at 25 C were investigated by equilibrating oils with water in open static tests. Limits of solubilities were established for the oils from results of long-term equilibration in closed vessels. Six oils were also equilibrated with salt water. A segmented mathematical model was derived and used to correlate experimental data. The model describes two processes that occur during equilibration: Soluble and volatile components of oil leach into solution initially and later evaporate.

Finally, a detailed description was made of the mass transfer processes occurring during chemical dispersion of oil spills. The primary mechanisms were quantified by analogy to homogeneous and heterogeneous catalysis and detergency. To evaluate the effectiveness of five commercial dispersants, a large-scale laboratory system was designed. Parameters investigated include oil and dispersant types, oil-to-dispersant ratio, degree of agitation, and the effect of salt water. The results of these evaluations indicate that the use of dispersants to control oil slicks must be based on knowledge of the action of specific chemicals.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Crude oils and petroleum-based products are extremely complex systems and behave differently when discharged to marine environments. Spills of chemicals that are less dense than water are usually marked by slick formation. Then several natural processes such as spreading and dissolution begin to act on the oil and cause it to disperse. Some processes operate on certain oil components more rapidly than others, and there are numerous interactions between the processes. The interactions are complex and poorly understood.

The rate of a specific dispersal process depends on a combination of factors such as oil type. To predict the fates of oils and their effects on the environment, it is necessary to quantify the rates of different dispersal processes for a variety of petroleum-based products with potential for spillage.

Spreading is one of the most important mechanisms causing dispersal of crude oils and petroleum products. The extent of the surface area of a spreading oil is a function of time and influences the rates of other dispersal processes. Thus

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knowledge of how fast oils spread on water is important to management decisions to control oil slicks. The rate of oil dissolution in water is useful for estimating hydrocarbon concentration levels in water to which marine organisms will be exposed. Although some research has been done on these dispersal processes, information is lacking on a variety of oils. An objective of this study was to investigate the spreading and dissolution behavior of nine crude oils and three petroleum-based products in laboratory experiments. Mathematical models were developed and used to correlate experimental data.

Although containment and physical removal are favored methods for controlling oil slicks, they are not practical in all spill situations. The use of nontoxic, chemical, surface-active agents is gaining wide acceptance.

The effectiveness of dispersants and their toxicity to marine life forms have been investigated many times, but laboratory results are not always consistent with field data because of poor test equipment and procedures. The effectiveness of five commercial dispersants was evaluated in this study during experiments conducted under controlled conditions in the laboratory. A major concern was the duplication of the mixing forces that exist in nature and field practices during chemical treatment of oil slicks.

This report identifies the mechanisms of oil/water/dispersant interactions, which are poorly understood. A comprehensive picture of chemical dispersion of oil slicks is presented, and mathematical descriptions of several fundamental processes are provided by analogy to partial detergency theory and catalysis.

Conclusions

Oily discharges to aquatic systems are usually marked by slick formation. Surface oil layers that form after spills have many undesirable impacts on the environment, such as aesthetic damage to beaches and shorelines, reduction of oxygen exchange at the air-water interface, fouling of wild fowl, etc. The potential for damage by oil spills depends on the rates of the dispersal mechanisms and other factors. Spreading and dissolution of oils in the underlying water are important dispersal mechanisms, but these rates have not been quantified for many petroleum-based systems. In this study, the rates of dissolution and spreading of 12 oils were investigated under laboratory conditions.

Spreading Rates for Oil Spills

Rates of spreading were determined experimentally by measuring the area covered and the time of small oil spills on calm water. Four different volumes of oils were spilled, and the areas covered by the slicks were determined photographically. Because the oils have different physical and chemical properties, the variables investigated included density, viscosity, surface tension, and interfacial tension between oil and water. Observations of the configurations of the spreading slicks indicated that the oils did not spread preferentially as rectangular, circular, or elliptical slicks. The shape of a slick generally varied according to the type of oil spilled, the rate of discharge, and other factors such as thermal convection currents and molecular motions in the water column.

Mathematical models were derived for oils spreading on calm water. The derivation of the spreading equations follows Fay's work. The principal forces influencing the spread of oils on calm water are gravitational, viscous, inertial, and net surface tension. Gravity accelerates spreading, causing the oil slick thickness to decrease and the oil to spread laterally. Viscous and inertial forces retard spreading, but the effect of the latter appears to be small. The net surface tension determines whether spreading is accelerated or retarded. These forces are related to the physical properties of the oil and water phases.

By equating an accelerating force to a retarding force, several spreading models containing only one empirical constant can be derived. The models fit the experimental data with varying accuracies. The order of goodness of fit, from best to worst, was generally as follows: gravity/viscous; surface-tension/viscous; gravity/inertia; and surface-tension/inertia. The surface-tension/inertia spreading model is independent of the volume spilled; this equation is not valid for predicting the areal extent of slicks. The effects of physical properties of the oil and water phases can be determined from the spreading equations. The effect of temperature on spreading rate was not investigated, but it can be determined from indirect influences on the physical and chemical properties of the oil and water phases.

Calm conditions do not persist indefinitely in the field, and ultimately, transport of gross oil by mechanical forces is superimposed on natural spreading. The interactions of wind, waves, and tides in the presence of oil slicks cannot be adequately simulated in the laboratory. The mechanical transport of oil as a result of these forces is probably more important than natural spreading in the overall dispersion of oil slicks if the damage to a coastline is considered. But the effects of these forces on oil slicks are known in general terms—oil slicks become elongated and distorted. Usually, the slick breaks into patches that drift in the direction of the wind at a speed proportional to the sum of the vector velocities created by transport forces. The influence of tides should be minimal because of the periodic and oscillatory nature of tidal movements.

Dissolution Rates

The dissolution rates of the oils were determined by measuring their solubilities in water during equilibration in open static tests. The oils were equilibrated with tap water at 25 C for 2 to 3 weeks. Experimental data show increases in oil concentrations initially and decreases later during the period of equilibration. Similar trends were exhibited by the experimental data generated by equilibrating six oils with salt water solution; however, solubilities were lower in tests with salt water, and the oils attained maximum solubilities at slower rates. Saturation data were determined from long-term, closed-system experiments. Solubilities vary for different oils and depend on oil composition. Organic species in solution were not characterized, but they are believed to be low-molecular-weight hydrocarbon compounds, e.g., aliphatics, aromatics, and substituted organics.

The experimental data suggest that as oil slicks equilibrate with water, volatile hydrocarbon species evaporate into the atmosphere from the air/oil interface, and soluble species dissolve into the underlying column of water from the oil/water interface. These processes are *not* in equilibrium; hydrocarbons continue to evaporate from solution after the oil layer has been depleted of volatile hydrocarbons. This process occurs even when oil is present in solution at less than saturation con-

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centrations. A segmented mathematical model was proposed to quantify the rates of dissolution for the duration of the equilibration period. This model consists of equations for the solution and evaporation phases. The model was used to fit experimental data. The results of the numerical simulation show that the model fits experimental data for a majority of the oils fairly well.

The conditions during the dissolution experiments correspond to an unlikely worst case of an oil spill in which the oil completely covers the water surface. Under these conditions, experimental data suggest that low concentrations of oil will persist in the water phase after 2 weeks of equilibration. In the field, the concentration of oil in the water column below surface slicks will be influenced by several factors, such as water quality. Dissolved organic matter is also present at varying concentrations in aquatic systems. Dissolved organic matter can solubilize organic compounds and increase oil concentration. Water movements will have a dilution effect on concentration, but it may cause oil droplets to be transported to the underlying column of water. Other processes that disperse and degrade petroleum operate simultaneously with dissolution. The concentration of oil in the aqueous phase will be influenced by the rates of these mechanisms.

Use of Chemical Dispersants

Management decisions to disperse oil spills with chemical dispersants must be based on knowledge of the action of commercial preparations and their toxicity to marine organisms. This study has identified the mass transfer processes that lead to the formation and dispersion of droplets in chemically treated oil slicks. Mathematical equations are proposed to quantify the rates of some of the principal mechanisms. These equations were not verified with experimental data, since necessary input data includes information that is considered proprietary or cannot be determined experimentally.

The efficiencies of five commercial products for dispersing three oils of varying physical and chemical characteristics were evaluated in a large-scale laboratory system. The design of the wave-tank was based on current dispersion practices, and the tank permits spatially distributed sampling. Variables investigated include oil-to-dispersant ratio, oil and dispersant types, and the effects of agitation and sea salts.

Experimental data show that efficiency increases with the volume of dispersant added. Oil concentrations decrease gradually with time after dispersion: The rate of decrease varied for each dispersant and oil combination. When the system is mixed continuously, agitation causes unstable and stable droplets to go initially into the aqueous phase. When agitation ceases, unstable droplets coalesce and migrate to the water surface. Oil concentration in the aqueous phase decreases with time and finally stabilizes. The dispersants are classified according to the efficiency of their action under test conditions by measuring the quantity of extractable organic materials in water samples.

The dispersal of spilled oil by application of chemical dispersants appears to be a promising method for cleaning up oil spills. Proper use of dispersants could result in the efficient dispersal of oil even in the absence of wave action. A gap in knowledge exists: the mechanism of dispersant action must be better understood, and the rates of spreading and dissolution must be established for a larger variety of crude oils and petroleum products.

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The complete report, entitled "Oil Slick Dispersal Mechanics," (Order No. PB 82-105 560; Cost: $24.50, subject to change) will be available only from:
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